## 1050. *Polyanion Equilibria in Aqueous Solution. Part I. The Quantitative Analysis of Acidified Tungstate Solutions.*

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A method for the quantitative analysis of acidified tungstate solutions by use of ^{185}W and paper chromatography has been developed. The equilibrium between the normal tungstate ion $WO_4{}^{2-}$ and the paratungstate A ion ($HW_6O_{21}{}^{5-}$), and the rate of formation of paratungstate B, have been studied.

THE species existing in acidified tungstate solutions have usually been investigated by observing the change in some physicochemical property as acid is progressively added to the solution of the normal tungstate, *e.g.*, by a study of pH,[1] conductivity,[2] temperature,[2b] vapour pressure,[3] Rayleigh turbidity,[4] light absorption,[5] and molecular weight (by cryoscopy,[6] diffusion,[7] or dialysis).[8] These measurements frequently indicate abrupt changes when either seven or nine equivalents of acid have been added to six moles of tungstate ion, $WO_4{}^{2-}$, corresponding to the formation of the paratungstate A ion $HW_6O_{21}{}^{5-}$ and the pseudo-metatungstate ion $H_3W_6O_{21}{}^{3-}$ respectively:

$$7H^+ + 6WO_4{}^{2-} = HW_6O_{21}{}^{5-} + 3H_2O$$
$$9H^+ + 6WO_4{}^{2-} = H_3W_6O_{21}{}^{3-} + 3H_2O$$
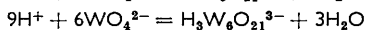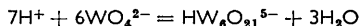
The existence of intermediate ions has also been claimed[9] and the results obtained by different workers do not always agree,[1f] both because of the large number of other species frequently present (*e.g.*, $W_3O_{10}{}^{2-}$ and paratungstate B) and the difficulty of obtaining solutions in equilibrium. Examination of paratungstate A solutions by absorption

[1] See, *e.g.*, (a) Britton, *J.*, 1927, 146; (b) Britton and German, *ibid.*, 1930, 1249; (c) Brintzinger and Ratanarat, *Z. anorg. Chem.*, 1935, **224**, 97; (d) Biehler, *Ann. Chim. (France)*, 1947, **2**, 489; (e) (i) Berkem, *Rev. Fac. Sci. Istanbul*, 1949, **14**A, 7; *Chem. Abs.*, 1950, **44**, 7179; (f) Jander and Kruerke, *Z. anorg. Chem.*, 1951, **265**, 244; (g) Pan and Hseu, *Bull. Chem. Soc. Japan*, 1953, **26**, 126; (h) Cannon, *J. Inorg. Nuclear Chem.*, 1960, **13**, 269; (i) Souchay, *Ann. Chim. (France)*, 1943, **18**, 61.
[2] See, *e.g.*, (a) Dumanski, Buntin, Dijatsch-kovski, and Kniga, *Kolloid Z.*, 1926, **38**, 208; (b) Jander and Heukeshoven, *Z. anorg. Chem.*, 1930, **187**, 60; (c) Pan, Lin, and Sheng, *Bull. Chem. Soc. Japan*, 1953, **26**, 131; also refs. 1b, d, e, g.
[3] Robinson and Sinclair, *J.*, 1934, 642.
[4] Bettinger and Tyree, *J. Amer. Chem. Soc.*, 1957, **79**, 3355.
[5] (a) Copaux, *Compt. rend.*, 1913, **156**, 1771; (b) Schulz and Spandau, *Z. phys. Chem.*, 1940, **185**, 325; (c) Jander and Spandau, *Z. anorg. Chem.*, 1927, **162**, 141; (d) Jander, Mojert, and Aden, *ibid.*, 1929, **180**, 129; (e) Jander and Jahr, *Kolloid-Beih.*, 1934, **41**, 1; (f) Iguchi, *Sci. Papers Coll. Gen. Educ., Univ. Tokyo*, 1957, **7**, 173, 183; also refs. 2b, 1f, h.
[6] Souchay, *Ann. Chim. (France)*, 1943, **18**, 169; also ref. 2a.
[7] (a) Herzog, *Z. Elektrochem.*, 1910, **16**, 1003; (b) Jahr and Witzmann, *Z. anorg. Chem.*, 1932, **208**, 145; (c) Anderson and Saddington, *J.*, 1949, S381; also refs. 5b, c, d, e.
[8] (a) Brintzinger and Brintzinger, *Z. anorg. Chem.*, 1931, **196**, 55; also ref. 1 (c); (b) Jander and Spandau, *Z. phys. Chem.*, 1940, A, **185**, 325; (c) Spitsyn and Pirogova, *Doklady Akad. Nauk S.S.S.R.*, 1957, **115**, 322.
[9] See refs. 1d, f, g, 2c.

8 M

spectroscopy,[1f] polarography,[10] dialysis,[8d] and chemical reactivity [11] shows that the para-tungstate A ion concentration decreases with time owing to the formation of the para-tungstate B ion, the exact nature of which is not known.

In 1953, Thilo and Grunze [12] separated the polyphosphate ions by paper chromatography. Murata [13] and Ripan *et al.*[14] have similarly separated the monomeric and the condensed forms of molybdate,[13,14] chromate,[13] vanadate,[13] and tungstate,[13] but no attempt was made to use the method quantitatively. Tungsten has been separated from other ions by ion-exchange at various pH,[15] by paper chromatography with acid solvents,[16] and on a column of 8-hydroxyquinoline [17] at pH 5—6, but in no case was separation of different tungstates noted. The object of this work was to develop a method of estimating polytungstate anions quantitatively by paper chromatography, and to use it to study the aqueous equilibria. The method used is similar to that employed by Ripan and Marcu,[18] but more species were evident in our work, and quantitative analysis for para-tungstate A in solutions of different pH was performed with an accuracy of $\pm 5\%$.

EXPERIMENTAL

Preparation of Solutions.—Radioactive sodium tungstate solutions were prepared by addition of a 10% molar excess of sodium hydroxide to "AnalaR" tungstic oxide which had been irradiated in B.E.P.O. at A.E.R.E., Harwell. The solution was filtered before use. All samples of tungstic oxide were allowed to decay for six months to eliminate any short-lived isotopes (^{187}W, ^{186}Re, ^{188}Re). After this time, conventional absorption methods showed only the presence of a 0·43 Mev β-particle (^{185}W, 0·428 Mev), with an additional 2% of detectable γ-activity (^{181}W). It may also be calculated that from the irradiation of natural tungsten there will also be produced about 0·001 μc of ^{182}Ta per mc of ^{185}W; this was ignored.

Control of pH.—The Cambridge pH-meter was standardised with carbonate-free 0·05M-potassium hydrogen phthalate and 0·01M-borax buffers. To obtain reproducible chromatographic behaviour it was essential to exclude carbon dioxide from all solutions. Otherwise, small changes in pH resulted which caused large changes in the composition of the tungstate solutions. Rigid precautions were also necessary to avoid absorption of carbon dioxide whilst the solutions were being pipetted, or transferred on to the paper. All experimental work was therefore carried out in a temperature-controlled glove-box, through which carbon-dioxide free air was maintained at a small positive pressure.

Chromatographic Technique.—A 5-μl. sample of the solution was pipetted on to a Whatman No. 1 filter-paper strip, 3 × 30 cm., at 5 cm. from one end. The chromatogram was developed by upward elution at 25° for 4 hr., with carbon dioxide-free 1 : 1 v/v water–ethyl alcohol. The pH of the eluate was not critical provided it was >4.

Measurement of Activity.—The dried chromatogram was placed in an automatic scanner which slowly moved it across a 3 mm. slit in an aluminium absorber (1 mm. thick) in front of a Geiger counter with a 7 mg./cm.² window. The output from the Geiger counter was fed into a ratemeter and a recording milliammeter, so that a continuous record of the radio-activity along the paper strip was obtained.

Two-dimensional Chromatography.—Although nearly complete separation of the components of a tungstate solution could often be obtained with unidimensional chromatography, there was usually appreciable tailing between the spots, because the rate of conversion of one species into another on the paper was not negligible. If, after the first unidimensional chromatogram was obtained, a second elution was made at right angles to the first, an estimate of the

[10] Souchay, *Ann. Chim. (France)*, 1943. **18**, 73.
[11] Jahr, *Naturwiss.*, 1941, **29**, 505; also ref. 10.
[12] Thilo and Grunze, *Sitzungsber. deut. Akad. Wiss., Berlin*, 1953, No. 5.
[13] Murata, *Nippon Kagaku Zasshi*, 1957, **78**, 57, 395; *Chem. Abs.*, 1958, **52**, 7006.
[14] Ripan, Duca, Paladi, Stanescu, and Mayer, *Bull. Soc. chim. (France)*, 1958, 1507, 1514.
[15] Iguchi, *Sci. Papers Coll. Gen. Educ., Univ. Tokyo*, 1956, **6**, 153; *Chem. Abs.*, 1957, **51**, 9255; Huffman, Oswalt, and Williams, *J. Inorg. Nuclear Chem.*, 1957, **3**, 49; Wilkins, *Talanta*, 1959, **2**, 355.
[16] See, *e.g.*, Kertes and Lederer, *Analyt. Chim. Acta*, 1956, **15**, 543; Majumdar and Mukherjee, *Analyt. Chim. Acta*, 1958, **19**, 480.
[17] Erlenmeyer and Dahn, *Helv. Chim. Acta*, 1939, **22**, 1369.
[18] Ripan and Marcu, *Studii si Cercetari Chim. (Fil. Cluj.)*, 1959, **10**, 17.

amount of interconversion occurring during the separation çould be obtained, and a correction made to the unidimensional chromatograms to obtain an accurate analysis of the mixture.

When the paper was dried after the first chromatographic separation, it was essential for the loaded part of the paper to be kept wet if the properties of the species were to remain unaltered. After the first elution of a piece (20 cm. square) of filter paper, the strip containing the tungsten was kept damp between two Polythene sheets, while the remainder of the paper was dried with an air-dryer. The Polythene sheets were then removed, and the second elution was carried out at right angles to the first. The whole area of the paper was then dried, cut into 1 cm. strips, and scanned. From the data obtained, Figs. 2 and 3 (see below) could be constructed.

Electrophoresis.—Sodium tungstate solutions were adjusted with aqueous sodium hydroxide or hydrochloric acid to a pH approximately the same as that of a chosen buffer solution. A sample was pipetted on to a paper-chromatographic strip and wetted with the buffer solution. A current of 6·1 milliamp. was passed along the paper for 6 hr. in an " Eel " electrophoresis apparatus. The movement of the tungsten along the paper was determined by scanning the paper for radioactivity as before (Whatman No. 1 chromatography strip). The field strength was variable (1—10 v/cm.).

It was essential that the ionic environment in acid and alkaline solutions should be closely similar if the relative mobility of the tungstate species in the two cases were to be validly compared. The concentrations of the acetate and ammonium buffers were therefore adjusted so that both had the same conductivity. Thus for pH $= pK_a$, the buffer concentrations were 0·100M for the ammonium buffer and 0·180M for the acetate buffer. Both were also made molar in sodium chloride.

Analysis.—Whilst there is no doubt that tungstate polymerisation occurs, an attempt was made to study the charge carried by the polyanion by direct analysis for tungsten and cation on the paper. The paper was divided and extracted with potassium hydroxide, and sodium, tungsten, and chloride were determined. In addition to the radioactive tungsten, radioactive hydrochloric acid (H^{36}Cl) was used to acidify the solution in these cases, and the movement of the chloride ion followed chromatographically in the same way as for tungsten. But since the separation of ^{185}W and ^{36}Cl by instrumental methods is not easy, it was necessary to perform a chemical separation before the radiochlorine contents of the paper sections could be determined. After the extraction with potassium hydroxide and the addition of tungstate and chloride carriers, cobalt tungstate was precipitated [19] at pH 9. It was centrifuged off, washed with water, mounted on a planchette, and radioactively assayed. Addition of fresh tungstate carrier, followed by a similar precipitation, ensured that the ^{185}W was completely removed. Silver chloride was then precipitated in acid solution and radioactively assayed in the same way.

Sodium was determined by flame-photometry after removal of the radioactive anions from the original potassium hydroxide extract by anion-exchange. Both the radioactive and the photometer results were standardised by normalising with respect to the total sodium, tungstate, and chloride ion known to be on the paper.

RESULTS AND DISCUSSION

Preliminary results show that above pH 9 most of the tungsten is present as one species (X). Fig. 1a shows a typical chromatogram with a single, well-defined spot at R_F 0·8. At lower pH (Fig. 1b) a second form (Y) appears (R_F 0·4), and the further the acidity increases the more Y increases at the expense of X, until at pH 5·0 the chromatogram is shown as in Fig. 1c. At still lower pH, another species (V) appears at high R_F values; in 0·1N-acid, tungstic oxide is precipitated, causing a well-defined peak (Z') at R_F 0 (Fig. 1e). Removal of tungstic oxide before chromatographic separation by centrifugation eliminates this component. At all pH, a species Z at R_F 0 (which is not WO$_3$) is found to increase slowly with time as shown in Fig. 1f, g, h.

(a) *Identification of Components.*—This chromatographic behaviour can be interpreted in terms of the generally accepted solution chemistry of tungsten as follows:
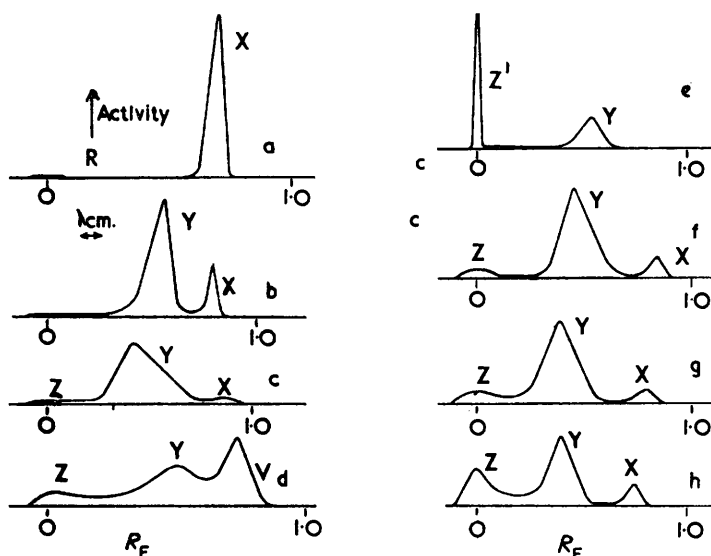
(i) In alkaline solution, the predominant species present (X) is assigned to WO$_4$$^{2-}$.

[19] Bradhurst, Coller, and Duncan, *J. Inorg. Nuclear Chem.*, 1957, **4**, 379.

This ion, having a relatively low charge and size, would be expected to have a high R_F value. (ii) As the acidity is increased, the first chromatographically separable species (Y) is assigned to the paratungstate A ion $HW_6O_{21}{}^{5-}$. The decrease in R_F value with increase of size and charge is to be expected by comparison with the chromatographic behaviour of polyphosphates,[20] polymolybdates,[14] and a variety of organic compounds.[21] (iii) Z is produced slowly from $WO_4{}^{2-}$ (X) and $HW_6O_{21}{}^{5-}$ (Y) and is taken to be the paratungstate B anion. There will, however, be a contribution from other species having a sufficiently high charge and/or large size to prevent movement along the paper. A chromatogram of freshly dissolved sodium paratungstate ($5Na_2O,12WO_3,28H_2O$) does not exhibit the same chromatographic behaviour as Z. It produces a sharp profile at $R_F = 0$, while Z produces a diffuse band, even in alkaline solutions. (iv) We believe species V to be the pseudo-metatungstate ion $H_3W_6O_{21}{}^{3-}$.

In some measure these assignments are confirmed by the fact that compounds Y, Z, and V show a blue colour on irradiation with ultraviolet light or sunlight, this fading

FIG. 1.   *Radioactivity profiles of* Na_2WO_4 *chromatograms.*

(a) pH 9·70, *zero time.*   (b) pH 6·77, *zero time.*   (c) pH 5·01, *zero time.*   (d) pH 2·53, *zero time.*
(e) pH 1·05, *zero time.*   (f) pH 6·23, *zero time.*   (g) pH 6·23, 2·2 *days.*   (h) pH 6·23, 6·5 *days.*

after 3 hours in the dark. This reaction is due to reduction of W^{VI} to lower-valency states [22] and has only been reported when acidified tungstate solutions are absorbed on paper.[1d] Since X is the only form not to show this reaction, it must be $WO_4{}^{2-}$, and the other peaks must be due to polymerisation.

(b) *Interconversion of Tungstates.*—The separation procedure was developed as a method of studying the equilibrium between $WO_4{}^{2-}$ and $HW_6O_{21}{}^{5-}$, which is complete in solution within 1—2 min. Nevertheless, the species can be separated by paper chromatography with very little interconversion during the process. For quantitative work, however, it is necessary that the degree of interconversion be known, and this was determined by two-dimensional chromatography. Fig. 2 shows a typical result from the two-dimensional chromatogram of a solution containing X ($WO_4{}^{2-}$), Y ($HW_6O_{21}{}^{5-}$),

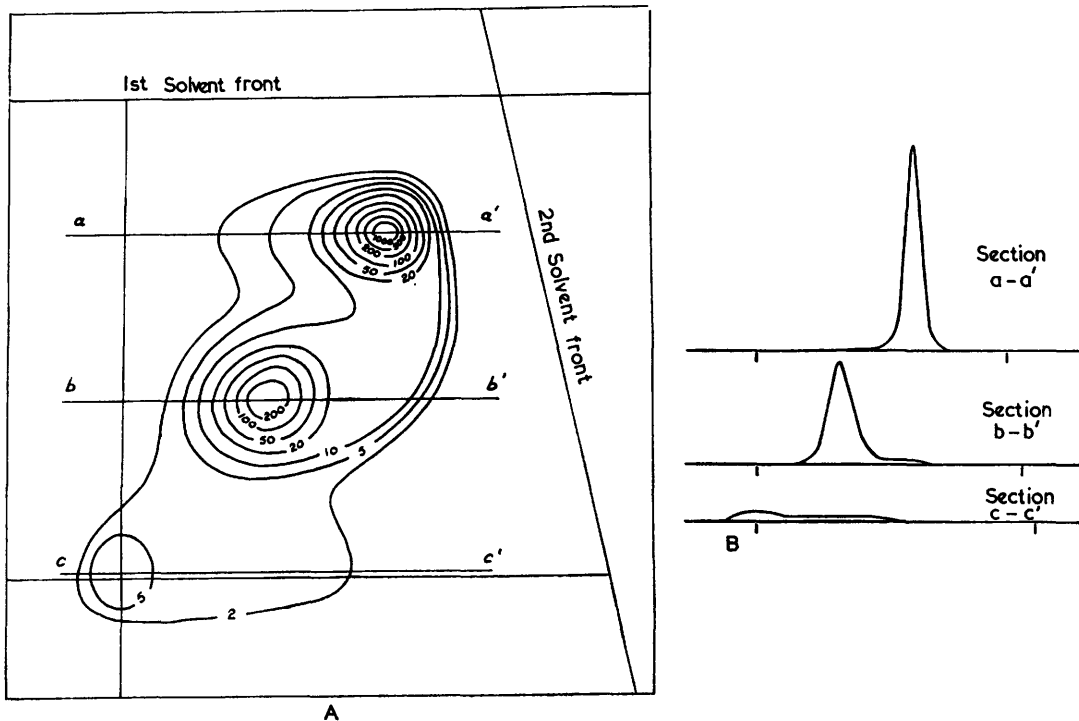[20] Thilo and Feldman, *Z. anorg. Chem.*, 1959, **298**, 316.
[21] Bate-Smith and Westall, *Biochim. Biophys. Acta*, 1950, **4**, 429.
[22] Bolliger and Hinks, *Austral. J. Sci.*, 1948, **11**, 60; Bolliger, *ibid.*, 1946, **9**, 166.

and Z (paratungstate B). By considering sections through the activity contours aa', bb', and cc' respectively, it can be seen that 1—2% of X (WO_4^{2-}) tails behind, 4—5% of Y ($HW_6O_{21}^{5-}$) appears as X, and Z (paratungstate B) produces a broad band along the paper as far as the front of Y. By means of these data the one-dimensional chromatograms can be corrected so that an accurate estimate of the quantity of each species present in the original solution may be made (see Fig. 3 for a typical case). The combined error from the statistics of counting, and in estimating the areas under the profiles, was less than $\pm 5\%$.

The interconversion between X (WO_4^{2-}) and Y ($HW_6O_{21}^{5-}$) is not unexpected, since equilibrium between the paratungstate A ion and the normal tungstate ion is reached

FIG. 2. (A) *Two dimensional chromatogram: contours are successively* 2, 5, 10, 50, 100, 200, 500, *and* 1000 *counts per min. per* 0·08 cm.² (B) *Activity profiles through sections* aa', bb', *and* cc'.

rapidly in solution. Nevertheless, effective separation can be obtained. Polymolybdates [14] and cadmium ammines [23] are other examples of chromatographic separation of the components of a rapidly established solution equilibrium.

For two species to be chromatographically separable, their rates of interconversion must be considerably retarded. One of the factors which affects the relative rates of reaction on a chromatogram, compared with those in solution, is the dielectric constant. The change in the rate constant, k, for the reaction between ions of charge Z_A and Z_B with dielectric constant (D) is given [24] by:

$$\frac{\partial \ln k}{\partial (1/D)} = -\text{Constant} \cdot Z_A \cdot Z_B$$

If the rate of the reaction which causes X to tail is proportional to $[H^+][WO_4^{2-}]$, *i.e.*,

[23] Erdmen and Erlenmeyer, *Helv. Chim. Acta*, 1954, **37**, 2220.

[24] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, N.Y., 1941, p. 430.

$Z_A Z_B = -2$, the rate in $1:1$ water–ethanol will be about one-fifth of that in water. On the other hand, if the rate of decomposition of Y ($HW_6O_{21}{}^{5-}$) is proportional to $[OH^-]$, *i.e.*, $Z_A Z_B = 5$, the rate of conversion into the normal tungstate ion would be expected to be about 100-fold faster than in water. Thus there would be a considerably greater conversion of paratungstate A into normal tungstate on paper than *vice versa*. Whilst the dielectric constant cannot be regarded as the only factor which can cause changes in reaction rate when the species are absorbed on paper, this prediction is in fact observed; but the interconversion rate is still less, by at least a factor of ten, than could be accounted for by the changes in dielectric constant alone.

(c) *Effect of* pH.—The concentrations of the different species in solutions of different

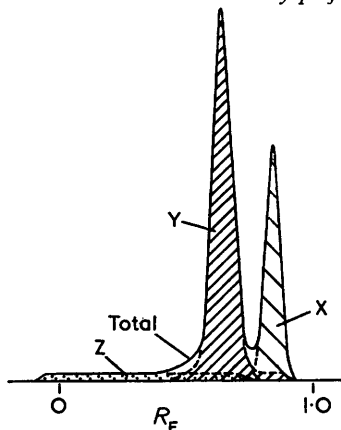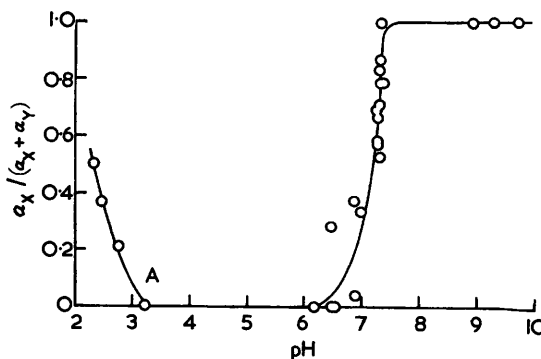FIG. 3. *Quantitative identification of components in a linear radioactivity profile.*

FIG. 4. *Dependence of composition upon* pH.

a_X and a_Y are the percentages of tungsten as $WO_4{}^{2-}$ and $HW_6O_{21}{}^{5-}$, respectively.

pH were determined by the chromatographic analysis of samples removed during the potentiometric titration at 25° of 2·00N-hydrochloric acid against 0·0192M-sodium tungstate containing a 10% (molar) excess of sodium hydroxide. Since the pH of acidified tungstate solutions increases slowly with time, all samples were kept overnight before measurement of the pH and chromatographic separation. The increased formation of component Z (paratungstate B) makes it undesirable to leave the solutions longer since this leads to increased tailing in the chromatogram and thus uncertainty in the quantitative analysis. There was found to be about 30% of component Z over the entire range of pH studied.

The results have been expressed in Fig. 4 by plotting $a_X/(a_X + a_Y)$ where a_X and a_Y are respectively the atom percentages of tungsten as $WO_4{}^{2-}$ and $HW_6O_{21}{}^{5-}$. Since it is not possible to distinguish between X and V by chromatography, any contribution from the latter will be included in a_X. In the pH range above 6—8, formation of V is not significant, but below pH 3·5 the presence of V undoubtedly accounts for the rising edge (A) of Fig. 4. Nevertheless it is apparent that the equilibrium $WO_4{}^2 \rightleftharpoons HW_6O_{21}{}^{5-}$ is markedly dependent on pH.

(d) *Time for Equilibration.*—The rate of formation of Z at 25° has been measured as a function of pH; a freshly acidified mixture of $\sim$0·1M-sodium tungstate with an $\sim$10% (molar) excess of sodium hydroxide was used for the kinetic studies. The results, shown in Fig. 5, are compared with similar results obtained by Souchay [10] by polarographic methods. Souchay approached equilibrium from both directions, first as in this work, and secondly by dissolution of solid sodium paratungstate [25] ($5Na_2O,12WO_3,28H_2O$) in water: he concluded that equilibrium is established in about one month. The chromatographic results, however, show that Z (paratungstate B) is still increasing in concentration even after

[25] Vallance, *J.*, 1931, 1421; Saddington and Cahn, *J.*, 1950, 3526; also ref. 1*i*.

this time. This suggests that Z also contains another polytungstate which is not intermediate in the formation of paratungstate A and paratungstate B, but is formed slowly from them. This would account for Dawihl's observation [26] that the solubility of ammonium paratungstate increases with time, equilibrium not having been established even after 14 months.

(e) *Properties of the Paratungstate A Anion.*—(i) pH *range of stability.* From Fig. 4 it can be seen that the paratungstate A ion, $HW_6O_{21}{}^{5-}$, is present in aqueous solution between pH 3·2 and 6·2. Above pH 7·5, the $WO_4{}^{2-}$ ion predominates, whilst below pH 3·2 there are appreciable quantities of the pseudo-metatungstate ion $H_3W_6O_{21}{}^{3-}$ (V) present. These results are analogous to the change [7] in self-diffusion coefficient between pH 5 and pH 9. It should be noted, however, that Souchay's polarographic results [10] are not in agreement with all the quantitative aspects of Fig. 4. In 0·1M-solutions (with respect to WO_3) he found 10% of the tungsten was present as the pseudo-metatungstate at pH 6·0 and about 90% at pH 5·0. This does not agree with our observation that in freshly prepared solutions this species is absent for pH >3·2.
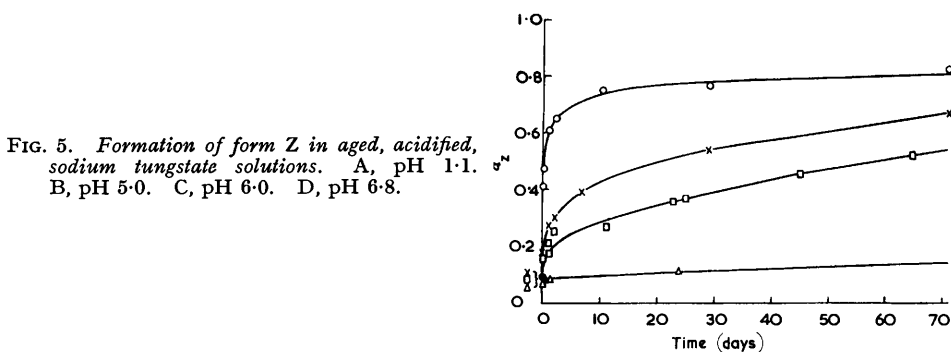

FIG. 5. *Formation of form Z in aged, acidified, sodium tungstate solutions.* A, pH 1·1. B, pH 5·0. C, pH 6·0. D, pH 6·8.

(ii) *Dimensions of the paratungstate A anion.* Anderson and Saddington [7b] found the self-diffusion coefficient of the normal tungstate anion to be $7·7 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ and of the paratungstate A anion to be $3·5 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. Recent electrochemical work [27] has shown that these results should be interpreted as due, not to a variation in mass, but to a variation in size. If the ions are considered as spherical balls, the radius calculated from Stokes's law or from Ottar's formula [27] is for $WO_4{}^{2-}$ 5·3 Å, and for $HW_6O_{21}{}^{5-}$ 12 Å. If the normal tungstate ion were tetrahedral, its unhydrated ionic radius would be about 2·9 Å. The average unhydrated radius of the condensed species is difficult to assess because of its unknown structure. If a 6-tungsten ring structure is assumed it would have a mean radius of about 5·0 Å, and the maximum radius across the ring would be about 5·8 Å. In comparing these figures, it should be noted that (*a*) both experimental figures are probably too high, since the self-diffusion coefficients determined by the capillary method are undoubtedly too low, perhaps even by a factor of 2 ; this would cause a greater relative error in the estimated radius for the condensed tungstate, for which mixing by diffusion would be less, and it would also explain the shallower slope of the plot of self-diffusion coefficient against pH [7c] than we obtained for $a_X/(a_X + a_Y)$ (Fig. 4), (*b*) both ions would be hydrated in solution, and the condensed ion may well be of sufficiently high charge to influence water molecules in more than the first hydration shell.

(iii) *Charge on the paratungstate A anion.* The relative mobility of the paratungstate A ion and the normal tungstate ion on paper was determined by electrophoresis. Although it is often asserted that this method gives an indication of the relative charges of the

[26] Dawihl, *Z. anorg. Chem.*, 1940, **244**, 1; *Chem. Abs.*, 1941, **35**, 2773.
[27] Ottar, *Acta Chem. Scand.*, 1955, **9**, 344; Stokes, *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 60; Baker and Pope, *J. Amer. Chem. Soc.*, 1960, **82**, 4176.

migrating species, we find it inapplicable to the present case. The results show that the tungsten does not move as far along the paper under acid as under alkaline conditions. Since the paratungstate A anion migrates more slowly than WO_4^{2-}, it is not possible to say whether it has a larger or a smaller charge. Undoubtedly the large difference in size contributes to this observation. A more direct method of estimating the charge of the paratungstate A anion was to analyse the chromatograms for sodium, tungstate, and chloride ion. The results are shown in Fig. 6. At high pH, the close proximity of the chloride to the WO_4^{2-} (Fig. 6a) caused the sodium to overlap both, making it impossible to decide how much sodium was associated with each component. The distribution of the sodium ions is unexpected, but the experimental error is sufficiently small for it to be real. The front of the chloride spot contains twice as much chloride as sodium, *i.e.*, it apparently contains free hydrochloric acid. The centre of the tungstate peak is sodium-deficient compared with Na_2WO_4. A similar effect is shown with a chromatogram of pure sodium chloride (Fig. 6b), where the chloride leads the sodium by about 1 mm. These chromatographic results are not, however, unique. Thilo [20] found a single peak

FIG. 6. *Analysis of chromatograms.* (a) *Sodium tungstate at* pH 8·08. (b) *Sodium chloride.* (c) *Sodium tungstate at* pH 7·55.

Arrows denote increasing number of moles (arbitrary scale). 1, Na^+. 2, WO_4^{2-}. 3, Cl^-.
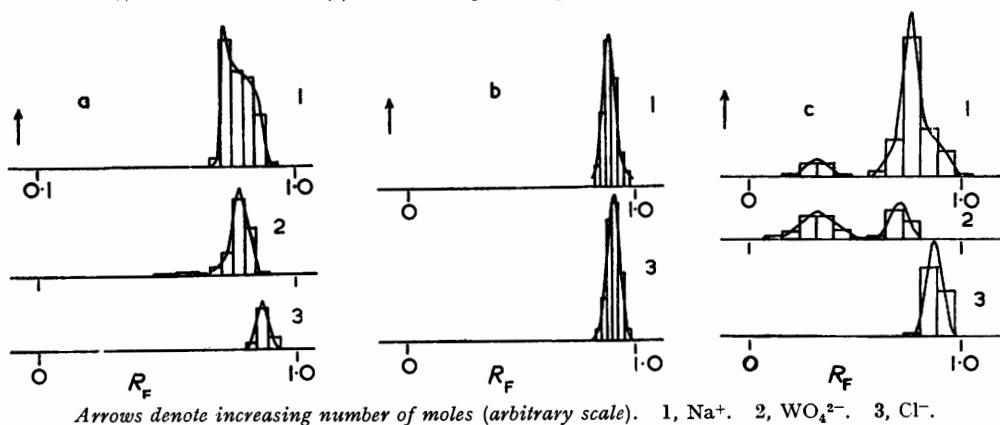
due to sodium in his separation of polyphosphates, even though about ten anionic components were separated.

It is thus impossible to estimate the charge on the polyanion from Figs. 6a and 6b. But at lower pH (Fig. 6c), where both the normal ion and the paratungstate ion are present, there are two sodium peaks. The first is between, but overlapping, both the chloride and the WO_4^{2-} peaks. The second is associated exclusively with the paratungstate A anion, appears to have uniform composition, and is well separated from the other components. We can with some confidence, therefore, use these results for determining the sodium : tungsten ratio as $(0·6 \pm 0·1) : 1$, *i.e.*, if form Y is the hexatungstate, its composition would be approximately $Na_{(3·5 \pm 0·5)}H_{(3·5 \pm 0·5)}W_6O_{21}$. Whilst the polytungstate ion can apparently be associated with three or four sodium ions on paper, the lack of a quantitative theory of paper chromatography makes it difficult to extrapolate this result into aqueous solutions. Nevertheless, it is clear that the polyanion must be highly charged ($Z > 3$) in water, and this is confirmed by theoretical electrochemical considerations. Under the conditions of Fig. 6c, the paratungstate anion would form a loose association with cations of the Bjerrum type; [28] and, if reasonable values for the ionic radius and the activity coefficients [29] are used at the concentrations employed for Fig. 6c, each polyanion would be associated with $3·8 \pm 0·3$ sodium ions.

[28] Robinson and Stokes, " Electrolyte Solutions," Butterworth, London, 1959, 2nd edn., p. 392.
[29] Duncan and Kepert, *J.*, in the press.

Conclusions.—It has been shown that the paper-chromatographic method of separation of the components of a polytungstate solution can be used for the quantitative analysis of the solution, provides auxiliary information about the structure and properties of the components, and can be done with milligrams or less of material. An important and general point is that this separation and analysis can be achieved even though the components are in rapid equilibrium in aqueous solution. Part II of this series [29] will deal with use of the method for quantitative investigation of the equilibrium between the normal tungstate anion and the paratungstate A anion, for which the free energy, enthalpy, and entropy changes have been evaluated, and certain possible modes of reaction eliminated.

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